

## Observation of change in the oxidation state at ferromagnet/insulator interface upon thermal annealing

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**Abstract.** – It is reported that the magnetoresistance (MR) of magnetic tunneling junction (MTJ) like  $\text{Co}_{1-x}\text{Fe}_x/\text{Al}_2\text{O}_3/\text{Co}_{1-x}\text{Fe}_x$  improves upon thermal annealing. We investigate the mechanism of this improvement by comparing the X-ray absorption spectra (XAS) of half-MTJ structures ( $\text{Co}_{84}\text{Fe}_{16}/\text{Al}_2\text{O}_3$ ) before and after annealing. Before annealing, XAS show the presence of few angstroms of Co- and Fe-oxides, which disappeared after annealing at 250 °C for 1/2 hour. We attribute enhanced MR upon annealing to the disappearance of Co and Fe oxides at the interface which reduce the spin-polarization of the conduction electrons and cause spin-flip scattering, both leading to inferior performance of MTJ.

Recent success in fabrication of magnetic tunneling junctions (MTJ) with magnetoresistance (MR) above 40% at room temperature has generated much interest because of their potential application as efficient magnetic random access memory (MRAM) [1]. MTJs are composed of two ferromagnetic (FM) electrodes separated by an insulating (I) layer with typical structures being  $\text{Co}_{1-x}\text{Fe}_x/\text{Al}_2\text{O}_3/\text{Co}_{1-x}\text{Fe}_x$ . It has been reported by several authors [1–5] that these recorded high MR values are obtained only after annealing the MTJ to 200–300 °C, which leads to increase in MR by  $\sim 30\%$  when compared to as-grown structures. This enhancement was correlated with the results of Rutherford backscattering (RBS) measurements [2,4], which indicated richer oxygen content at FM/I interface in the as-grown sample and homogeneous distribution of oxygen after the sample is annealed to 200 °C. This is suggestive of partially oxidized ferromagnetic electrode in the as-grown sample resulting in degradation of the MR, which is subsequently removed upon annealing. However, RBS

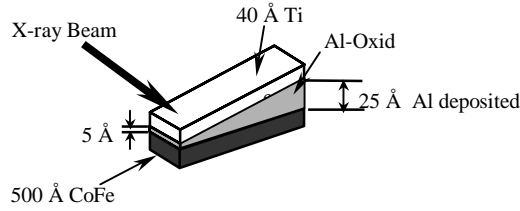


Fig. 1 – Schematic drawing of the  $\text{Co}_{84}\text{Fe}_{16}/\text{Al}_2\text{O}_3$  wedge structure together with the experimental geometry.

experiments cannot directly observe the oxidation states of the interfacial FM layers or their disappearance upon annealing. We use X-ray absorption spectroscopy (XAS) to address this issue by directly monitoring the chemical states of FM in  $\text{Co}_{84}\text{Fe}_{16}/\text{Al}_2\text{O}_3$  bilayer before and after annealing process. The XAS spectra at the  $L_3$ -edge of  $3d$  transition metal elements and their oxides exhibit different, easily distinguishable features, which makes XAS an ideal tool to investigate the oxidation states of FM electrodes in MTJ. We employ a bilayer consisting of Al wedge in order to perform a systematic study of the effect of annealing as a function of  $\text{Al}_2\text{O}_3$  thickness. This is of particular importance since the  $\text{Al}_2\text{O}_3$  barriers of MTJ are fabricated by oxidation of Al layers and the optimal FM/I interface should have all of the Al and none of the FM oxidized. Another difference between the RBS study and the one presented here is that we probe the bottom FM/I interface while the RBS work concentrated on the top FM/I interface of the FM/I/FM structure. Our results demonstrate clearly that the Co and Fe oxide observed in the as-grown structures can be completely removed by annealing to  $250^\circ\text{C}$  for optimal Al thickness. Further annealing to higher temperature ( $350^\circ\text{C}$ ) did not cause any change in the oxidation state at the FM/I interface.

The samples for the XAS experiments were fabricated at IBM Almaden Research Center by magnetron sputtering. A  $200\text{ Å}$  of  $\text{Co}_{84}\text{Fe}_{16}$  was first deposited on a silicon wafer followed by an aluminum wedge of  $5\text{--}20\text{ Å}$  thickness deposited over a distance of  $23\text{ mm}$  using computer-controlled mask. The Al wedge was then plasma oxidized in an oxygen atmosphere for 600 seconds, and capped by  $40\text{ Å}$  of Ti subsequently to protect it from further oxidation in the air. The sample structure is schematically shown in fig. 1. XAS measurements were performed at the Advanced Photon Source high-resolution intermediate X-ray spectroscopy facility (beamline 2ID-C) located at Argonne National Laboratory. Co and Fe  $L$ -edges and Al  $K$ -edge absorption spectra were collected in total yield mode at locations of different Al thickness along the wedge (see fig. 1). The photon energy resolution was  $100\text{ meV}$  for Co and Fe measurements and  $250\text{ meV}$  for Al XAS with an X-ray spot size of  $0.25\text{ mm} \times 2\text{ mm}$ . The sample was annealed *in situ* twice with e-beam bombardment, first to  $250^\circ\text{C}$ , then to  $350^\circ\text{C}$ . Spectra before and after heating were compared to reveal the effects of annealing.

Figures 2 and 3 show the Co  $L_3$ -edge and Fe  $L_3$ -edge absorption spectra, respectively, before and after annealing for different Al overlayer thickness. Since the Al wedge is grown on top of the  $\text{Co}_{84}\text{Fe}_{16}$  layer and then exposed to the oxygen plasma, it can be expected that at thinner side of the Al wedge the  $\text{Co}_{84}\text{Fe}_{16}$  underlayer may be partially oxidized. This is clearly evident in the spectra. Figure 2(a) shows Co  $L_3$  XAS of the as-grown sample. The spectra taken at the thin side of the Al wedge ( $t_{\text{Al}} = 5.7\text{ Å}$ ) show a mostly Co oxide lineshape while the spectra taken at  $t_{\text{Al}} = 14.1\text{ Å}$  clearly show metallic Co. Although the Co  $L_3$  spectra of Co oxide and Co mostly overlap in energy, they do have very different spectral lineshapes. The Co oxide spectrum exhibits peaks at  $777.7\text{ eV}$ ,  $778.2\text{ eV}$ ,  $778.8\text{ eV}$  and a pre-edge peak at  $776.3\text{ eV}$  while the metallic Co structure is a single broad peak centered at  $777.7\text{ eV}$ . In particular,

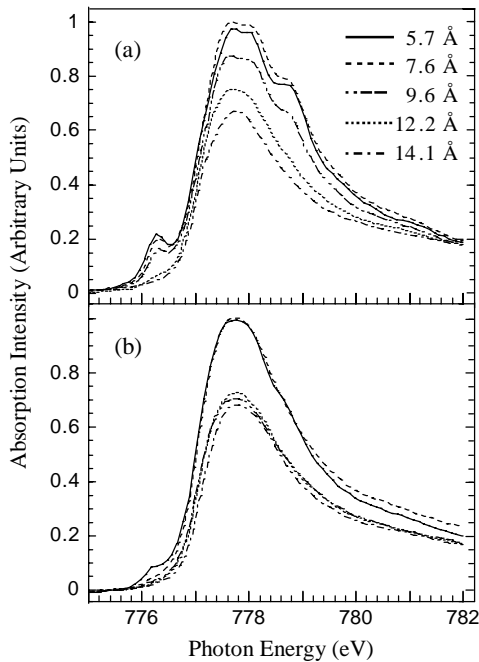


Fig. 2

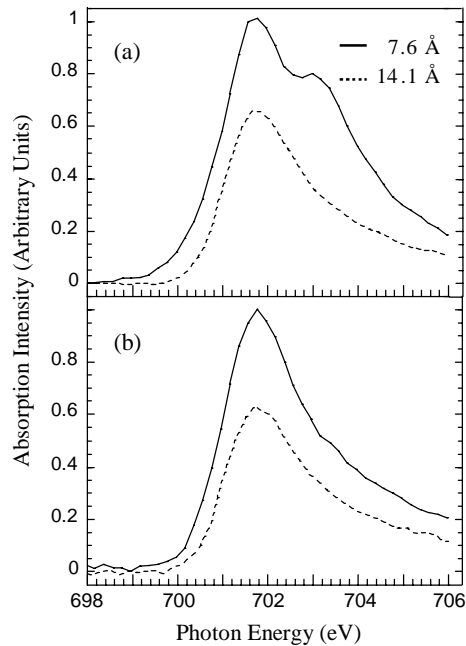


Fig. 3

Fig. 2 – Co  $L_3$ -edge X-ray absorption spectra before (a) and after (b) the first annealing (250 °C for 1/2 hour). Spectra are taken at different positions along the Al wedge which corresponds to different Al thicknesses as indicated.

Fig. 3 – Fe  $L_3$ -edge X-ray absorption spectra before (a) and after (b) annealing (250 °C for 1/2 hour) as in fig. 2. Spectra taken along the Al wedge at two different Al thicknesses are shown.

only the Co oxide exhibit the pre-edge peak at 776.3 eV which we use later for quantitative analysis. Similar conclusions can be reached by looking at the Fe  $L_3$ -edge spectra in fig. 3(a), although here we recorded only two spectra, one at the thin and the other at the thick end of the Al wedge. The Fe  $L_3$ -edge spectra of metallic Fe is a single-peak structure centered at 701.7 eV, while the Fe oxides lineshapes are notably broader and centered at  $\sim 703$  eV. Thus the spectra in figs. 2(a) and 3(a) suggest that both Fe and Co oxide concentrations at the interface reduce as the thickness of Al layer increases. These changes are rather pronounced because the probing depth of the Co  $L_3$  XAS ( $\sim 50$  Å) is just beyond the thickness range of the Ti plus Al layers so that only the top part of the Co is being sampled.

Figure 2(b) and 3(b) present a set of Co and Fe  $L_3$ -edge absorption spectra, respectively, after the sample was annealed to 250 °C for half an hour. It is evident that the amount of oxide present before annealing (figs. 2(a) and 3(a)) has diminished considerably. In fig. 2(b), only a very small amount of Co oxide, identified by a small pre-edge shoulder, is present at the very thin end of the Al wedge ( $t_{Al} = 5.7$  Å). The annealing clearly reduces the amount of interfacial oxide present in the ferromagnetic  $\text{Co}_{84}\text{Fe}_{16}$  electrode to zero, except at the very thin Al layers. Since the most predominant phases of both Co and Fe oxides exhibit antiferromagnetic order, they are expected to considerably reduce the MR effect in MTJ because of both i) decrease in the conduction electron spin polarization at the FM/I barrier and ii) spin-flip scattering. The magnetic tunneling junctions of type  $\text{Co}_{84}\text{Fe}_{16}/\text{Al}_2\text{O}_3/\text{Co}_{84}\text{Fe}_{16}$  prepared with an identical

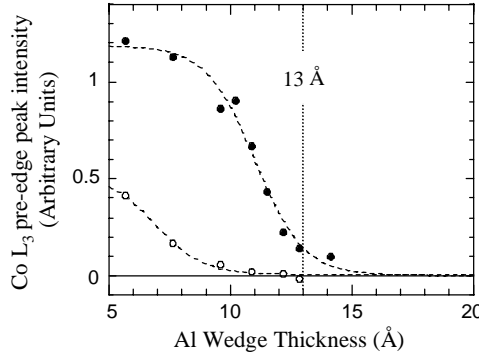


Fig. 4 – Co  $L_3$  pre-edge peak intensity at 776.3 eV as a function of Al wedge thickness before (filled circles) and after annealing (open circles). The dashed line is a fit to an empirical formula:  $[1 + \exp[t/t_0]] - 1$ .

fabrication procedure as the structures studied here do show that annealing to  $\sim 230^\circ\text{C}$  increases the MR by more than 30% [1]. Thus we suggest that a direct cause of the observed MR enhancement is the reduction of the amount of Co- and Fe-oxide at the FM/I interface.

In order to examine more quantitatively the effects of annealing on interface chemistry, in fig. 4 we plot the amount of Co oxide as a function of wedge position before and after annealing. For this we use the intensity of the pre-edge peak (776.3 eV) of the Co  $L_3$  spectra before (filled circles) and after (opened circles) annealing from the data in figs. 2(a) and 2(b), respectively. The dashed lines are fits to an empirical lineshape of the form  $[1 + \exp[t/t_0]] - 1$ . A large reduction of Co oxide after annealing is clearly seen. For as-grown films and for a given oxidation time, the Co oxide is expected to be present only if the Al layer is thinner than the corresponding oxidation depth. The Al oxidation depth for an identical Al-wedge sample oxidized for 600 s was determined in a previous IR reflectivity study to be 13.5 Å [6]. This is in excellent agreement with a current study which shows no Co oxide beyond  $\sim 13$  Å in the as-grown sample (indicated as a vertical dashed line in fig. 4). The annealing to  $250^\circ\text{C}$  reduces the amount of Co oxide throughout the wedge (open circles). Most notably, the Co oxide completely disappears at the FM/I interface for Al thickness larger than  $\sim 9$  Å. Since an optimal MTJ uses a barrier made of 10-15 Å Al, this figure nicely demonstrates how annealing completely removes the interfacial Co oxide present after the fabrication of these junctions. Upon subsequent annealing to  $350^\circ\text{C}$  for another 1/2 hour no further change occurred in the XAS spectra of Co or Fe  $L$ -edge. This is in agreement with recent experiments [5] in which the degrading of MTJ performance after high-temperature annealing was attributed to the interfacial diffusion at exchange biased antiferromagnetic/ferromagnetic interface rather than to the change at FM/I interfaces.

The observed disappearance of Co and Fe oxide upon annealing can be understood from a thermodynamics argument since the heat (or enthalpy) of formation of Al oxide is more than five times that of Co or Fe oxide, which suggests that the Al oxide is much easier to form and more stable than the Co or Fe oxide. Therefore during the annealing process, the small amount of oxygen bonded to Co and Fe can be captured by Al especially if the amount of Co and Fe oxide is small. We estimate the oxidation of the  $\text{Co}_{84}\text{Fe}_{16}$  layer to be on the order of 2 Å, which would be consistent with this picture.

We now turn to study the insulator layer ( $\text{Al}_2\text{O}_3$ ) of the sample before and after annealing ( $250^\circ\text{C}$ ) by examining a set of Al  $K$ -edge absorption spectra shown in fig. 5. Similar to the

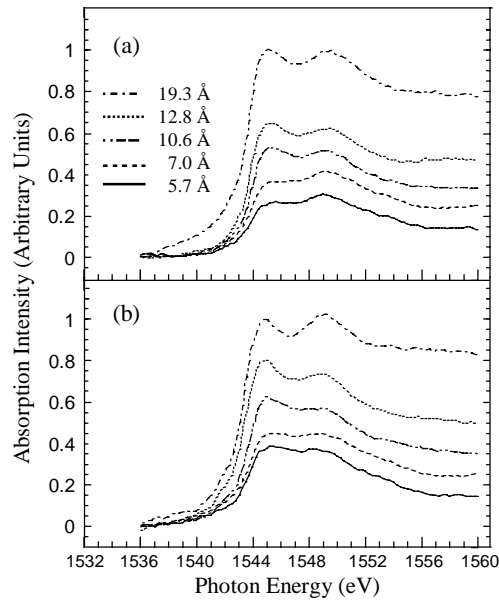


Fig. 5 – Al  $K$ -edge X-ray absorption spectra from as-grown sample (a) and after annealing (250 °C for 1/2 hour) (b) at different Al thicknesses along the wedge.

previous analysis of Co data, the spectra are recorded at different positions of the wedge corresponding to different Al layer thicknesses. A comparison of the spectra before annealing (fig. 5(a)) indicates very little change across the wedge, apart from the overall intensity. On closer inspection, however, we observe a slight change in the relative intensity of the two main peaks of the Al  $K$ -edge absorption, which we ascribed to slight changes in the Al environment. These differences are somewhat reminiscent of the small difference in the Al  $K$ -edge absorption spectra of  $\alpha$ - and  $\gamma$ - $\text{Al}_2\text{O}_3$ . It is interesting to point out that the most notable changes occur at  $\sim 10$  Å, which is close to the point where the Co interface layer changes from oxide to metal as determined above. The annealing process appears not to change the spectra, except that the above-noted changes in the Al  $K$  ratio observed before annealing appear to now occur at thinner Al thickness, tracking with the point where the Co interface changes from oxide to the metal, as determined earlier from the Co  $L_3$  spectra. However, we note that comparison among different spectra is difficult because of changes in the absorption background. We would also like to point out that all the measured Al  $K$  absorption spectra are considerably broader than the one from sapphire suggesting a large degree of coordination disorder in these barriers.

In summary, we have investigated the effects of annealing on the chemical composition of the FM/I interface by observing the oxidation state change in a CoFe/ $\text{Al}_2\text{O}_3$  wedge structure. Annealing to 250 °C for 1/2 hour removes most of Co and Fe oxides in the  $\text{Co}_{84}\text{Fe}_{16}$  layer resulted from 600 s plasma oxidation on 5–25 Å of Al overlayer. This directly explains the increase in the MR effect after annealing in MTJs made of similar structure. The annealing did not appear to change the state of the Al oxide layer as monitored by Al  $K$ -edge absorption, except for a slight change of lineshape with the wedge thickness. Annealing to a higher temperature of 350 °C did not result in further change of the chemical state of the ferromagnetic layer. Our results provide important guidelines for the manufacturing and processing of MTJs.

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